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# Chromophore Ordering by Confinement into Carbon Nanotubes

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## Abstract

We report an experimental study on the confinement of oligothiophene derivatives into single-walled carbon nanotubes over a large range of diameter (from 0.68 to 1.93 nm). We evidence by means of Raman spectroscopy and transmission electron microscopy that the supramolecular organizations of the confined oligothiophenes depend on the nanocontainer size. The Raman Radial Breathing Mode frequency is shown to be monitored by both the number of confined molecules into a nanotube section and the competition between oligothiophene/oligothiophene and oligothiophene/tube wall interactions. We finally propose simple Raman criteria to characterize oligothiophene supramolecular organization at the nanoscale.

Keywords: Supramolecular organization, Single wall carbon nanotubes, Dimethyl-quaterthiophene, Raman, TEM.

## Introduction

Single-walled carbon nanotubes (NTs) have a one-dimensional hollow space varying from 0.4 to 2.0 nm and that can encapsulate various molecules.<sup>1</sup> In these nanohybrid systems, the

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physical properties of the molecules are supposed to be strongly influenced by their confinement in the one-dimensional cavity and by their specific interactions.<sup>2-3</sup> For example, members of the fullerene family inserted inside nanotubes give rise to  $\pi$ - $\pi$  interactions which are expected to stabilize the guest-host structures.<sup>4</sup> Calculations have also suggested that confinement of molecules inside NTs can induce structural phase transitions not seen in the bulk phase.<sup>5-8</sup>

Functionalization of nanotubes with organic molecules has attracted significant attention owing to the possibility to modulate NTs properties.<sup>9</sup> These molecules have been envisaged for optoelectronics<sup>10</sup> or electron-transport devices<sup>11</sup> as they display outstanding photophysical properties. Unfortunately, they often suffer from low stability and poor electrical characteristics.<sup>10</sup> Thus, endohedral functionalization is an efficient way to overcome these drawbacks. One advantage of the encapsulation is that the nanotube protects the internal organic molecules from photo degradation and attacks by external reactive species, thereby preventing undesirable alteration of the organic molecules.<sup>12</sup> Recently, several experimental works dealt with the encapsulation of oligothiophene derivatives (oTh) into NTs (oTh@NT).<sup>13-15</sup> Indeed, these systems are particularly interesting as the  $\pi$  conjugation of the thiophene molecules provides nonlinear optical properties and intrinsic electrical conductivity.<sup>16-20</sup>

Recent DFT calculations<sup>21</sup> reported that the electronic states added by the terthiophene molecules inserted into carbon nanotubes would give rise to original optical effects and non radiative relaxation from excited states. Concerning the structure of the nanohybrid material, Yamashita *et al.* predict that internal thiophene oligomers prefer to be located near the walls of the armchair nanotubes rather than close to the axis.<sup>22-23</sup> Furthermore, total energy

calculations suggest that the van der Waals interaction between the oligothiophene and the tube is stronger than the intermolecular interaction.<sup>13</sup> The different theoretical works suggest a correlation between the structural organization of the guest molecules and the size of the tubes. Nevertheless, up to now, no experimental evidence of such a correlation over a wide range of nanotubes diameter has been reported.

In this work, we investigate experimentally the dependence of the structural properties of NTs filled with methyl-terminated quaterthiophene (4T, figure 1 in supporting information) as a function of the nanotube diameter. We performed a systematic study of hybrid nanotubes in a diameter range from 0.68 to 1.93 nm using Raman spectroscopy and high resolution transmission microscopy. We found out that 4T molecules inside nanotubes form different structures depending on the NT diameters. Different critical diameters are identified, controlled by the interactions between guest thiophene molecules and host nanotube and confined 4T-4T interactions.

## **EXPERIMENTAL :**

**Sample preparation:** Four sources of nanotubes have been used in this study: commercial electric arc single-walled carbon nanotubes ( $1.2 \text{ nm} < d < 1.6 \text{ nm}$ ), provided by Carbon Solution<sup>24</sup> and called NT14 in the following; carbon nanotubes synthesized by the EDiPS method<sup>25</sup> ( $1.6 \text{ nm} < d < 2 \text{ nm}$ ) (NT18 in the following); HiPCO carbon nanotubes ( $0.6 \text{ nm} < d < 1.2 \text{ nm}$ ),<sup>26</sup> called NT09 in the following and CoMoCAT carbon nanotube enriched in (7,6) nanotubes ( $0.6 \text{ nm} < d < 1 \text{ nm}$ ),<sup>27</sup> NT08 in the following. HiPCO, Carbon Solution and CoMoCAT nanotubes were purified by air oxidation and subsequently treated to remove the catalyst. The eDiPS nanotubes were purified according to the following protocol: 20 mg of raw SWNT material were sonicated in nitric acid (35 vol. %) (150 mL) with a sonic bath (160 W max) (100% for 5 min and then 40% for 15 min) and then heated at 100°C for 5h. The

suspension was then cooled and vacuum filtered through a PTFE membrane (Sartorius, 0.2  $\mu\text{m}$ ). While pursuing vacuum filtration, the thick SWNT layer formed on the filtration membrane (buckypaper) was washed by 200 ml of deionized water; pH was monitored during the washing and is about 7 at the end of the process. The nanotubes were redispersed in NaOH 1M (100 mL) using the sonic bath (100% for 10 min) and then filtered through a PTFE membrane and washed with NaOH 1M, deionized water and then HCl 1M followed by deionized water until the filtrate was neutral. Finally, the bucky paper was redispersed in hydrogen peroxide (30 %) (150 mL) using the sonic bath (100% for 5 min and then 40% for 10 min). The suspension was heated at 100°C for 1 h, cooled down at room temperature and then vacuum filtered through a PTFE membrane. The nanotubes were washed by 200 ml of deionized water and then dried at 50°C under high vacuum. The overall yield of the purification process was 60 % (12 mg).

Encapsulation of 4T into carbon nanotubes is performed using the vapour reaction method previously described.<sup>15</sup> Before the encapsulation treatment, carbon nanotubes are outgassed at 300°C for 48 hours. Then, NTs are mixed with 4T-CH<sub>3</sub> in weight ratio:  $w_{\text{NTS}}/w_{\text{4T-CH}_3}=0.5$ , in glove box and outgassed under  $2.10^{-6}$  mbar at ambient temperature for 1 hour. Then, NTs with 4T are sealed in glass tube at  $2.10^{-6}$  mbar and heated to 250°C for 72 hours. Sublimation step is then performed. The sample was then washed with organic solvent and stored in the oven at 120°C for 24 hours. The hybrid material is named 4T@NT in the following.

**Raman spectroscopy: Micro** Raman experiments have been performed on a triple monochromator spectrometer (Jobin Yvon T64000), equipped with a charge-coupled detector, in a back scattering geometry, using the fixed 457.9, 488.0, 514.5, 568.2 and 647.1 nm excitation wavelengths and a Ti-Sapphire tunable source in the near infrared region. The spot size is around few microns in diameter probing an ensemble of nanotubes.

In order to prevent the heating of the tubes and oligomers, the laser power was adjusted at 100  $\mu\text{W}$  with a spot diameter of about 3  $\mu\text{m}$  using a 50X objective. The resolution is about 2  $\text{cm}^{-1}$ . At least four spatially separated area of each sample were probe to ensure homogeneity.

**HR-TEM:** The TEM samples were prepared by dispersing the NTs powders in ethanol. The dispersions were ultrasonicated and subsequently deposited on a holey carbon 3 mm copper grids. TEM images were made using two TEMs: a ZEISS Libra 200 MC operating at 200 kV was used to study different sources of nanotubes. A Cs-corrected JEOL ARM200 CC operating at 80 kV was used to quantify precisely the encapsulation.

### **Computational details:**

DFT calculations were performed with the SIESTA package<sup>28</sup> on a 4T@(11,0). In this model, we use a (11,0) nanotube of 29.82 Å length (diameter of 8.6 Å) with periodic conditions along its axis. The vacuum size was of 11 Å in the two other directions to avoid interactions between adjacent tubes. The guest molecule is a quaterthiophene oligomer bounded with methyl groups (4T). The first Brillouin zone was sampled using 8 *k*-points along the nanotube axis. The atomic positions were relaxed at fixed lattice parameters using a conjugate gradient until the maximum residual force on the atoms was smaller than 0.02 eV/Å. Exchange-correlation effects were handled within the generalized gradient approximation (GGA) as proposed by Perdew, Burke and Ernzerhof.<sup>29</sup> Core electrons are replaced by nonlocal norm-conserving pseudopotentials.<sup>30</sup> The valence electrons were described by localized pseudoatomic orbitals with a double- $\zeta$  singly polarized (DZP) basis set.<sup>31</sup> The cutoff radii for the *s* and *p* orbitals were respectively 4.99 and 6.25 a.u. for the carbon atoms, and 4.97 and

6.22 a.u. for sulfur atoms, whereas it was 6.05 a.u. for the *s* orbital of hydrogen atoms. A real space integration was performed on a regular grid corresponding to a plane-wave cutoff around 300 Ry. We also use van der Waals corrections (DFT-D) between the tube and the guest molecule according to the Grimme approach.<sup>32</sup> This approach consists in adding a semi-empirical dispersion potential (a simple pair-wise force field) to the conventional Kohn-Sham DFT energy.

## **RESULTS AND DISCUSSION :**

Raman spectra of carbon nanotubes are very sensitive to charge transfers and/or environmental effects,<sup>33-34</sup> making thus possible to investigate very efficiently the interaction between oligothiophene molecules and nanotubes. The G-band undergoes significant modifications after 4T encapsulation associated to a charge transfer, already discussed in reference 15.

Here, we will focus on the low frequency region located between 80 and 350 cm<sup>-1</sup> where the Radial Breathing Modes (RBM) related to the tube diameters are observed. The relationship between the frequency  $\omega$  and the tube diameter  $d$  is usually given by the following equation:

$\omega(\text{cm}^{-1}) = A/d(\text{nm}) + B$  where  $A$  and  $B$  are two constants.<sup>33-43</sup> The following relationship

$d = \frac{217,8}{\omega_{\text{RBM}} - 15,7}$  from the reference<sup>40</sup> is used in this work to determine the carbon nanotube diameters.

Figure 1 displays the Raman spectra in the RBM frequency range at different laser excitation wavelengths for empty nanotubes (open circles) and 4T@NT samples (full squares). The diameter distribution is strongly dependent on the nanotube source. The modes clearly exhibit a frequency up-shift after encapsulation for different laser excitation energies. The relative up-shifts ( $\Delta\omega_{\text{RBM}} = \omega_{\text{RBM}}(4\text{T@NT}) - \omega_{\text{RBM}}(\text{NT})$ ) for all the nanotubes investigated are plotted on

figure 2 as a function of the NT diameter and the different excitation wavelengths. The behavior is clearly non-monotonic and displays a complex dependence with the nanotube diameter over the whole range.

For small diameter NT, typically between 0.68 and 1.1 nm, the relative up-shifts are almost constant. This trend is well characterized by a plateau around a value of  $2\text{ cm}^{-1}$  for  $\Delta\omega_{RBM}$ . A linear behavior is observed for diameters between 1.1 and 1.4 nm. Another plateau can be also considered between 1.4 and 1.65 nm, suggesting that the RBM shifts are independent of the NT diameter in this range. To confirm this assumption, a detailed study of the RBM frequency shifts in this diameter range for the encapsulation into NT14 carbon nanotubes of other kinds of oligothiophenes (quaterthiophene ( $\alpha$ -4T), sexithiophene ( $\alpha$ -6T) and dimethyl-quaterthiophene (4T)) is displayed on the inset of figure 2. Those data indicate that the relative RBM up-shift upon encapsulation is rather constant around a value of  $7.5\text{ cm}^{-1}$  in this diameter range whatever the nature of the confined molecules. Finally, for diameter larger than 1.6 nm the behavior is shown to be linear despite the low number of experimental points.

The RBM behaviors can be associated to the amount of molecules confined into a nanotube section and their supramolecular organization as suggested by experimental work on water encapsulation<sup>44</sup> and theoretical studies on sexithiophene into nanotubes.<sup>13</sup>

To study the structural organization of the nanohybrid systems, we performed HRTEM measurements on 4T@NT. Figure 3 displays some representative HRTEM micrographs of carbon nanotubes with different diameters filled with 4T (left) and their corresponding contrast profiles (right). Concerning the smallest carbon nanotube, we can distinguish three minima in the contrast profile of figure 3.d. The minima on the sides correspond to the carbon nanotube walls. The minimum in between is reasonably associated to a 4T molecule confined inside the carbon nanotube. The observed configuration is one isolated chain inserted in the



carbon nanotube and centered along the nanotube main axis. For the nanotube with a diameter of 1.4 nm, two minima are located in between the NT walls. Thus, the configuration in this case consists in two molecular chains inserted in the same nanotube section.

For the largest carbon nanotube (figure 3c), one can observe three minima in between the nanotube walls (figure 3f), showing that a third chain is inserted. Thus, to explain the RBM shifts as a function of the nanotube diameter, we propose the model described below. For diameter between 0.68 and 1.1 nm, only one single molecule fit in the tube. Indeed, the oligothiophene width is around 0.48 nm for an isolated molecule in its most stable structure, when adjacent rings are non-parallel to one another thanks to a rotation around the connecting bond. Furthermore, the van der Waals distance to the tube wall is roughly 0.32 nm,<sup>13</sup> so that a 1.1 nm diameter tube can accommodate only one molecule ( $0.48 + 2 \times 0.32 = 1.12$  nm). Below 1.1 nm, we assume that the oligothiophene size is strongly reduced under nano confinement by aligning all the thiophene rings to form a nearly planar structure. This hypothesis is supported by our calculations. Indeed, after relaxation, the 4T molecule inside a (11,0) nanotube displays dihedral angles between thiophene rings smaller than  $1.1^\circ$  and its distance to the nanotubes wall is 4 Å (figure 4.a). Therefore, a planar molecule can incorporate nanotubes with diameter down to 0.68 nm, as experimentally observed. Our calculations also predict that 4T molecules cannot enter a (8,0) nanotube (diameter  $d = 0.63$  nm) as no stable configuration is found out. Therefore, the critical NT diameter for 4T encapsulation is around 0.65 nm.

For nanotubes diameter between 1.10 and 1.45 nm, a second chain is inserted (figure 4.b). DFT calculations for 4T confined into a (17,0) nanotube (diameter = 1.35 Å) give the following structural parameters: the distance between the two molecules is 6.5 Å whereas the distance between the molecules and the tube wall is 3.4 Å, close to the inter-sheet distance in graphite (figure 4.b).

Around 1.1 nm, the molecules are very close to each other and strongly interact, leading to a slight upshift. When the NT diameter increases, the molecules get further and further away, interacting more and more with the NT wall, giving rise to the linear behavior observed on figure 2. This assumption is consistent with theoretical works since the molecules are calculated to be more and more distant as the nanotube diameter increases as a consequence of a higher affinity of the molecule with the nanotube walls.<sup>10, 13, 45-48</sup> Between 1.40 and 1.65 nm, the NT diameter is large enough to accommodate only two molecules close to the wall. Beyond 1.65 nm, the insertion of a third molecule is possible and the distance to the nanotube wall decreases when the tube diameter increases.

The RBM shifts induced by non-covalent endohedral functionalization of nanotubes with different species can have different origins such as dispersive interactions, charge transfer, mechanical strain... For fullerene molecules ( $C_{60}$ ,  $C_{70}$ ,  $C_{76}$ ...), the dispersive interactions (van der Waals), generally lead to a small down-shift (2 or 3  $\text{cm}^{-1}$ ) according to the reference Britz and Khlobystov<sup>49</sup> and references therein. However, the shift direction could depend on the nanotube diameter as reported by S. Okada<sup>50</sup> and S. Joung et al.<sup>51</sup> Indeed, encapsulation into large diameter tubes (above 1.37 nm) leads to a down-shift due to an electronic hybridization between NT and  $C_{60}$  whereas insertion into smaller diameter tubes leads to a small up-shift caused by a steric hindrance. Charge transfer (positive or negative) onto individual metallic nanotubes has been shown to induce a small RBM up-shift of about 2  $\text{cm}^{-1}$  due to a renormalization effect as observed for the Raman G-band.<sup>52</sup> This behavior is observed when electron acceptor molecules are encapsulated into bundles of semiconducting or metallic tubes<sup>49</sup>. By contrast, insertion of electron donor species such as alkali metals gives rise to a small down-shift for lithium,<sup>53</sup> no shift for rubidium<sup>54</sup> and a slight up-shift for cesium.<sup>55</sup> As the 4T molecule is an electron donor, the physical interactions with the nanotubes are

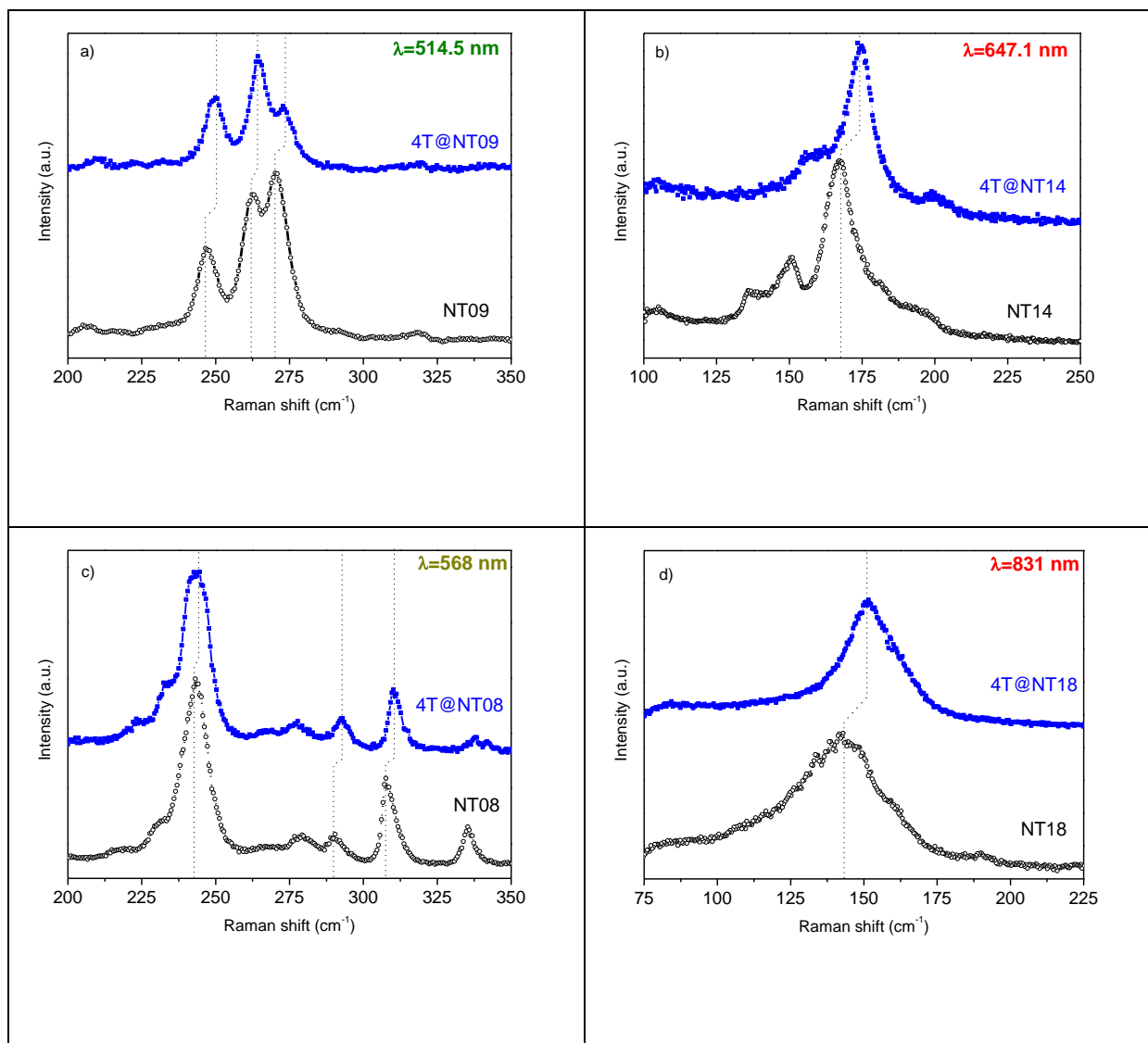
probably dispersive and combined to a slight charge transfer (as evidenced in ref.15). It is worth mentioning that the RBM shifts are at most  $-3\text{ cm}^{-1}$  for dispersive interactions<sup>49-51</sup> and  $+2\text{ cm}^{-1}$  for charge transfer.<sup>52,55</sup> Thus, for 4T confined into NT, one can reasonably expect RBM shifts in this wavenumber range or close to zero if both interactions cancel each other. However, figure 2 displays RBM shifts that reach  $+8\text{ cm}^{-1}$  at the second plateau and up to  $+17\text{ cm}^{-1}$  for the largest diameter tube. Then, the behavior of the RBM shifts over the large diameter range cannot be simply understood as a superposition of dispersive interactions and charge transfer. H. Kataura et al. interpreted the RBM behavior of nanotubes (shifts of about  $+5\text{ cm}^{-1}$  and intensity reduction) after Zn-diphenylporphyrin encapsulation (good electron donor<sup>49</sup>) as a nanotube deformation due to the large size of the molecule (1 nm).<sup>56</sup> We therefore believe that the 4T molecules induce a mechanical strain on the nanotubes whose energy depends on the amount of molecules confined and on the closeness between the 4T and the NT. This closeness depends on the NT diameter as suggested by our DFT calculations.

Thus, according to our Raman investigations, the magnitude of the RBM upshifts as a function of the nanotube diameter is governed by two different parameters: the number of confined molecules lying in a nanotube section and the physical interaction taking place either between the molecules themselves or between the molecules and the nanotubes walls.

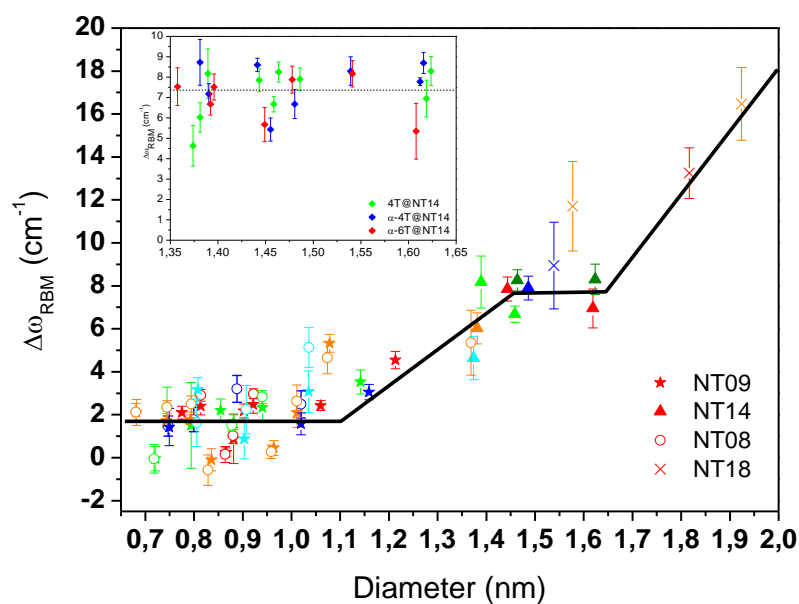
## Conclusion

In summary, combined Raman and HRTEM measurements allow to determine the supramolecular organization of 4T confined into single-walled carbon nanotubes. We evidence different critical nanotubes diameters. Below 1.1 nm, only one molecule is encapsulated. Between 1.1 and 1.6 nm, two oligothiophenes are confined. Above 1.6 nm, three molecules are inserted. The Raman Radial Breathing Mode frequency displays a

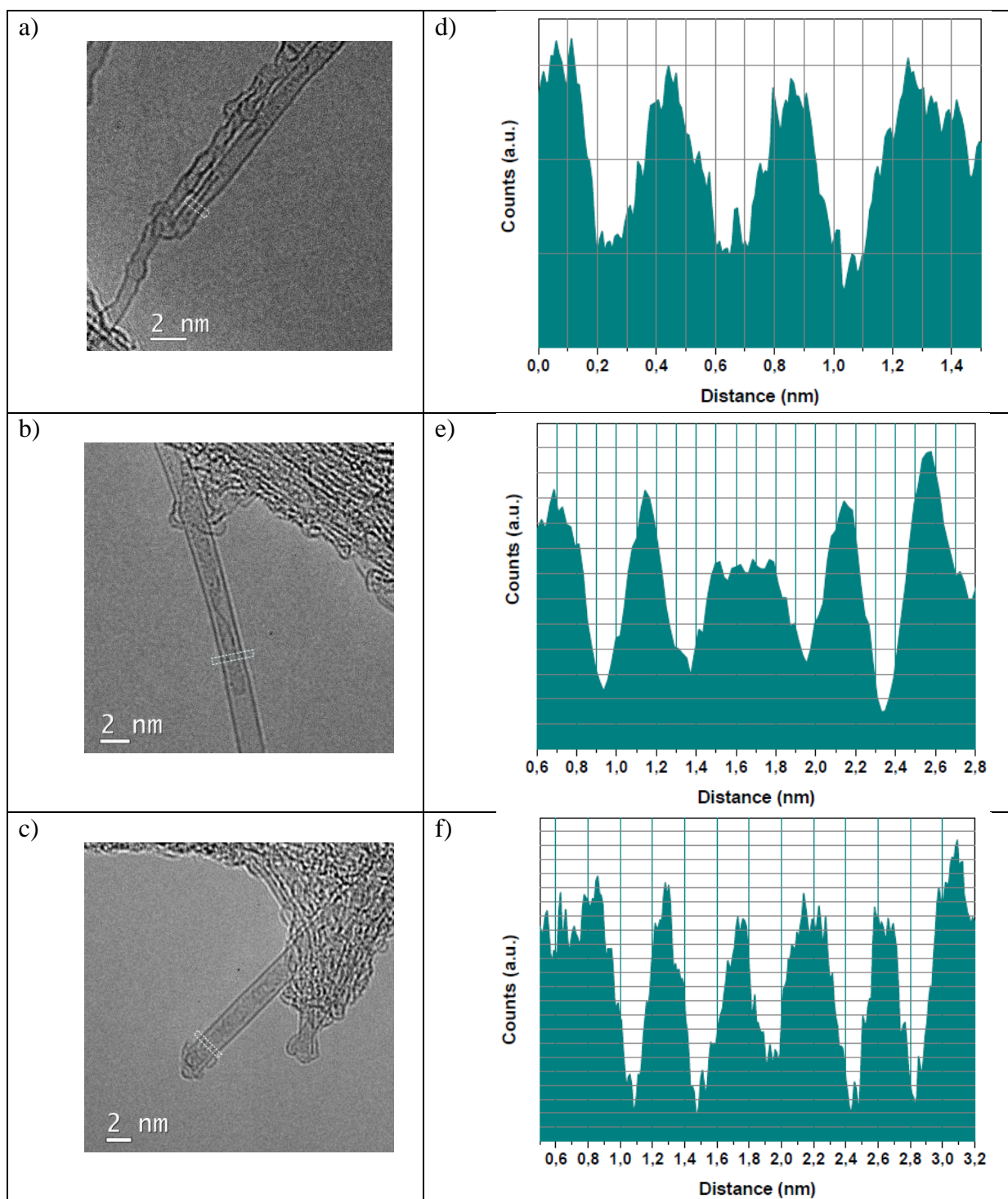
nonmonotonic behavior with the NT diameter. It turns out to be monitored by both the number of confined molecules into a nanotube section and the competition between oligothiophene/oligothiophene and oligothiophene/tube walls interactions. Our results allow establishing simple Raman criteria to characterize oligothiophenes supramolecular organization at the nanoscale by investigating carefully the magnitude of the RBM up-shifts. To go further in our investigations, nanotubes with specific diameters are required. For instance, diameters around 1.3 nm would allow obtaining more experimental points in the linear regime. Diameters larger than 2 nm would allow reaching the third plateau which should correspond to three molecular chains interacting with the nanotubes walls without any interaction between the molecules themselves.



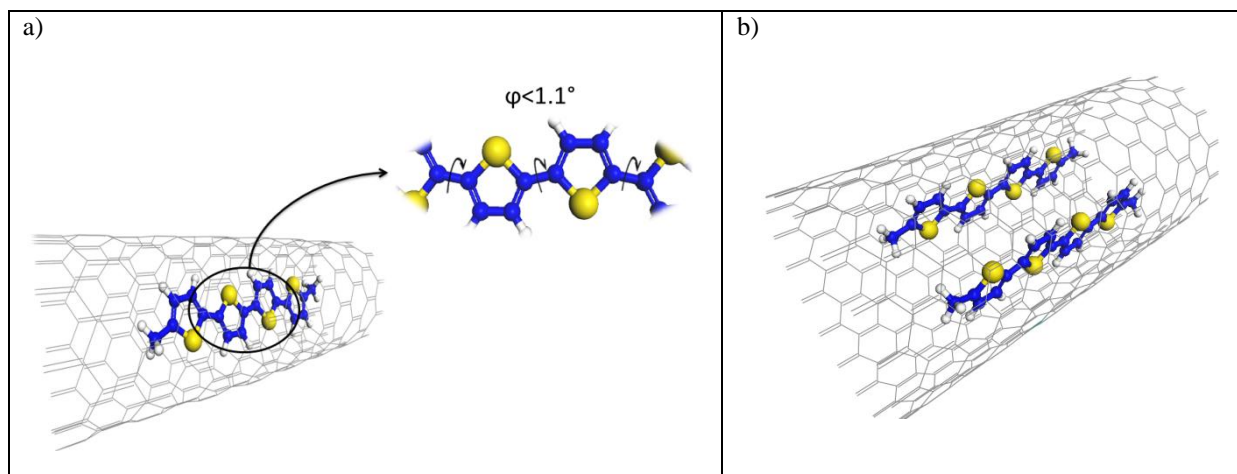
**Figure 1:** Raman spectra of NT and 4T@NT in the RBM range recorded at different laser excitation wavelengths



**Figure 2:** RBM relative up-shifts after encapsulation of 4T molecules inside NT08 (open circles), NT09 (stars), NT14 (triangles) and NT18 (crosses) carbon nanotubes. The colors of the symbols correspond to the laser excitation wavelengths (cyan=458 nm, blue=488 nm, dark green=532 nm, green=514.5 nm, red=647.1 nm, orange=568 nm). The black straight lines are guide for eyes. **Inset:** RBM relative up-shifts after encapsulation of oligothiophene molecules (4T, α-4T and α-6T) inside NT14 carbon nanotubes.



**Figure 3:** (a,b,c) HRTEM micrograph of carbon nanotubes with different diameters filled with 4T molecules. (d,e,f) Contrast profiles (along the rectangle) of the left carbon nanotubes



**Figure 4:** Optimized 4T@NT structures for a (11,0) tube (a) and a (17,0) tube (b)

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#### Supporting Information available:

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